

Methyl 4-[[*(1Z)*-1-benzoyl-3-oxo-3-phenylprop-1-en-1-yl]amino]benzoate

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Key indicators

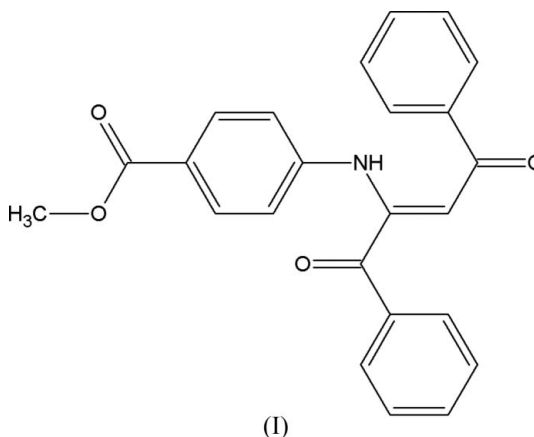
Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.061
 wR factor = 0.144
Data-to-parameter ratio = 17.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{24}\text{H}_{19}\text{NO}_4$, was obtained as a by-product in the synthesis of 1-phenyl-4-nitrophenylpropane-1,3-dione. The crystal structure is stabilized by several inter- and intramolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

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Comment

β -Diketone complexes of transition metals have been the subject of many different studies ranging from synthetic (Pedersen *et al.*, 1959; Weinmayr, 1958), kinetic (Leipoldt, Basson *et al.*, 1991; Leipoldt, Lamprecht & Steynberg, 1991; Leipoldt & Grobler, 1986) and structural (Roodt *et al.*, 1992; Ferguson *et al.*, 1994; Haaland & Nilsson, 1968; Yogev & Mazur, 1967) topics to catalysis (Cullen *et al.*, 1991; Cullen & Wickenheiser, 1989) and many others (Stary, 1964; Mehrotra *et al.*, 1978). Our research involves the synthesis of β -diketones with different functionalities (du Plessis *et al.*, 1999) and the complexation of these β -diketones to metals (Lamprecht *et al.*, 1993; Conradie *et al.*, 2002, 2005) for use in the study of model catalyst systems. In an attempt to synthesize 1-(4-nitrophenyl)-3-phenylpropane-1,3-dione to be used as bidentate ligand, crystals of the title compound, (I), were obtained.



In the molecule of the title compound, (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

Rings *A* (C3–C7), *B* (C11–C16) and *C* (C19–C24) are, of course, planar and the dihedral angles between them are $A/B = 74.70(4)^\circ$, $A/C = 11.59(3)^\circ$ and $B/C = 71.55(3)^\circ$. This preferred conformation could be the effect of the intramolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ and intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions (Table 1), which may be effective in the stabilization of the crystal structure. Dipole-dipole and van der Waals interactions are also effective in the molecular packing.

Experimental

The title compound was obtained as a by-product in the synthesis of 1-phenyl-4-nitrophenylpropane-1,3-dione. The reaction was performed under Schlenk conditions. Lithium diisopropylamide (6.70 ml, 10.0 mmol, 1.5 M) was added to a stirred solution of acetophenone (98%, 1.226 g, 10.0 mmol) in THF (1.0 ml) with cooling in an ice-bath. The resulting transparent brown–orange solution was stirred for a further 20 min at 273 K. Methyl 4-nitrobenzoate (1.8115 g, 10.0 mmol) was added and the reaction mixture was stirred overnight at room temperature (293 K), resulting in a milky brown solution. Diethyl ether was added, resulting in a thick brown–yellow suspension. The precipitate was filtered off and acidified by dissolving it in HCl (50 ml, 0.3 M). The product was extracted with diethyl ether (3 × 50 ml). The combined extracts were washed thoroughly with water, dried (MgSO₄) and the solvent removed under reduced pressure. Chromatography of the residue on kieselgel 60 (*R_F* = 0.18) with hexane–diethyl ether (5:1) as eluant afforded a mixture of 1-phenyl-4-nitrophenylpropane-1,3-dione and the title compound. The title compound was obtained by fractional recrystallization from DMF.

Crystal data

C₂₄H₁₉NO₄ *Z* = 4
M_r = 385.4 *D_x* = 1.365 Mg m^{−3}
 Monoclinic, *P*₂₁/*n* Mo *K*α radiation
a = 10.0396 (5) Å *μ* = 0.09 mm^{−1}
b = 9.8912 (5) Å *T* = 100 (2) K
c = 18.9631 (9) Å Block, yellow
β = 94.965 (3)° 0.2 × 0.13 × 0.09 mm
V = 1876.04 (16) Å³

Data collection

Bruker X8 APEXII 4K 13970 measured reflections
 diffractometer 4606 independent reflections
 φ and ω scans 3462 reflections with *I* > 2σ(*I*)
 Absorption correction: multi-scan *R_{int}* = 0.046
 (*SADABS*; Bruker, 2004) *θ_{max}* = 28.4°
T_{min} = 0.982, *T_{max}* = 0.992

Refinement

Refinement on *F*² *w* = 1/[σ²(*F_o*²) + (0.0588*P*)²
R[*F*² > 2σ(*F*²)] = 0.061 + 0.8797*P*]
wR(*F*²) = 0.144 where *P* = (*F_o*² + 2*F_c*²)/3
S = 1.08 (Δ/σ)_{max} < 0.001
 4606 reflections Δρ_{max} = 0.34 e Å^{−3}
 267 parameters Δρ_{min} = −0.27 e Å^{−3}
 H atoms treated by a mixture of independent and constrained refinement

Table 1 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N—H1...O4	0.88 (2)	1.99 (2)	2.703 (2)	138 (2)
C1—H1B...O3 ⁱ	0.98	2.55	3.068 (2)	113
C1—H1C...O2	0.98	2.31	2.671 (3)	101
C4—H4...O2 ⁱ	0.95	2.49	3.368 (2)	154
C5—H5...O3 ⁱⁱ	0.95	2.46	3.386 (2)	165

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y, -z + 1$.

The amine H atom was located in a difference syntheses and refined isotropically. The remaining H atoms were positioned geometrically, with C—H = 0.95 and 0.98 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms,

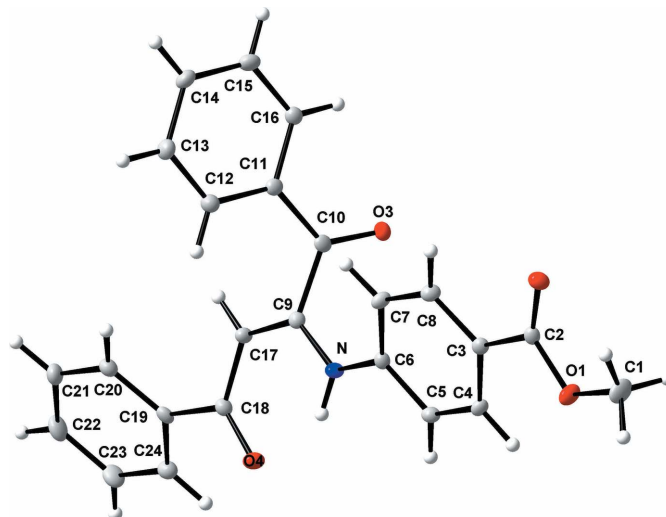


Figure 1 The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

with *U_{iso}*(H) = *xU_{eq}*(C), where *x* = 1.2 for aromatic and *x* = 1.5 for methyl H atoms.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Altomare, A., Burla, M. C., Camalli, M., Casciarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
 Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Release 3.1b. Crystal Impact GbR, Bonn, Germany.
 Bruker (2004). *SADABS* (Version 2004/1) and *SAINT-Plus* (Version 7.12 including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2005). *APEX2*. Version 1.0-27. Bruker AXS Inc., Madison, Wisconsin, USA.
 Conradie, J., Cameron, T. S., Aquino, M. A. S., Lamprecht, G. J. & Swarts, J. C. (2005). *Inorg. Chim. Acta*, **358**, 2530–2542.
 Conradie, J., Lamprecht, G. J., Otto, S. & Swarts, J. C. (2002). *Inorg. Chim. Acta*, **328**, 191–203.
 Cullen, W. R., Rettig, S. J. & Wickenheiser, E. B. (1991). *J. Mol. Catal.* **66**, 251–251.
 Cullen, W. R. & Wickenheiser, E. B. (1989). *J. Organomet. Chem.* **370**, 141–154.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Ferguson, G., Glidewell, C. & Zakaria, C. M. (1994). *Acta Cryst.* **C50**, 1673–1676.

- Haaland, A. & Nilsson, J. (1968). *Chem. Commun.* pp. 88–89.
- Lamprecht, G. J., Swarts, J. C., Conradie, J. & Leipoldt, J. G. (1993). *Acta Cryst. C* **49**, 82–84.
- Leipoldt, J. G., Basson, S. S., van Zyl, G. J. & Steyn, G. J. J. (1991). *J. Organomet. Chem.* **418**, 241–247.
- Leipoldt, J. G. & Grobler, E. C. (1986). *Transition Met. Chem.* **11**, 110–112.
- Leipoldt, J. G., Lamprecht, G. J. & Steynberg, E. C. (1991). *J. Organomet. Chem.* **402**, 259–263.
- Mehrotra, R. C., Bohra, R. & Gaur, D. P. (1978). *Metal β -Diketonates and Allied Derivatives*, pp. 268–277. London: Academic Press.
- Pedersen, C. J., Salem, N. J. & Weinmayr, V. (1959). US Patent No. 2 875 223.
- Plessis, W. C. du, Erasmus, J. C., Lamprecht, G. J., Conradie, J., Cameron, T. S., Aquino, M. A. S. & Swarts, J. C. (1999). *Can. J. Chem.* **77**, 378–386.
- Roodt, A., Leipoldt, J. G., Swarts, J. C. & Steyn, G. J. J. (1992). *Acta Cryst. C* **48**, 547–549.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stry, J. (1964). *The Solvent Extraction of Metal Chelates*. New York: MacMillan Company.
- Weinmayr, V. (1958). *Naturwissenschaften*, **45**, 311–311.
- Yogev, A. & Mazur, Y. (1967). *J. Org. Chem.* **32**, 2162–2166.